

Appendix B: Evidence Supporting the Irreversibility of Sulfur's Emission Impact

Fuel sulfur impacts vehicle emissions in two basic ways. One is an immediate impact, which occurs within a few miles of driving. The other is a more lasting impact, ranging from 20 or more miles to potentially permanent. This lasting effect of sulfur on emissions is termed irreversibility, referring to the fact that the emission impact of high sulfur fuel does not reverse when low sulfur fuel is used.

The immediate impact of sulfur on emissions is summarized in an EPA technical report.¹ There, it was shown that operation on typical conventional gasoline containing 330 ppm sulfur increases exhaust VOC and NOx emissions from LEV and Tier 2 vehicles (on average) by 40 percent and 150 percent, respectively, relative to their emissions with certification fuel containing roughly 30 ppm sulfur. All of the data supporting these impacts were generated with very short exposures to high sulfur gasoline, essentially a few miles of preconditioning and a few miles of actual emission testing. When the vehicles were tested using low sulfur fuel after being operated on high sulfur fuel, special preconditioning was performed to ensure that any residual effect of the high sulfur fuel was removed. This preconditioning would not normally occur through normal vehicle operation, so the emission impacts described in Section III only strictly apply to situations where the vehicle operated on fuel with a single sulfur level over its entire life.

In this section, we are concerned with the impact of sulfur under more realistic conditions. In particular, we are interested in vehicles' emission response following exposure to low sulfur fuel after exposure to high sulfur fuel. We are also concerned with the potential that long term exposure to high sulfur fuel may increase emissions to a greater degree than the short term exposures simulated in most emission testing.

This section is divided into five parts. The first section describes the sensitivity of vehicle exhaust emissions to gasoline sulfur content. The second discusses the theory of how sulfur affects catalytic activity and the conditions conducive for its removal (sulfur reversibility/irreversibility). The third describes the vehicle testing programs which have attempted to measure the reversibility of the sulfur impact. This part also compares the relative impact of long term sulfur exposure versus short term exposure. The fourth presents criteria for evaluating the wide range of sulfur reversibility data which are available. Finally, the fifth describes EPA's projections of the degree of sulfur reversibility for various vehicle types (e.g., Tier 1 vehicle, LEVs, and Tier 2 vehicles).

A. Exhaust Emission Sensitivity to Sulfur Content

The sulfur in gasoline increases exhaust emissions of HC, CO, and NOx by decreasing

Tier 2/Sulfur Draft Regulatory Impact Analysis - April 1999

the efficiency of the three-way catalyst used in current and advanced emission control systems. For the purpose of this document, we will refer to this phenomenon as “sulfur sensitivity.” Sulfur sensitivity has been demonstrated through numerous laboratory and vehicle fleet studies. These studies have demonstrated that significant reductions in HC, CO, and in particular, NO_x emissions can be realized by reducing fuel sulfur levels. Sulfur sensitivity for Tier 0 and Tier 1 vehicles is marginal, with NO_x emissions decreasing between 11 percent to 16 percent when sulfur is reduced from 330 ppm to 40 ppm. Sulfur sensitivity for LEV and ULEV vehicles, however, is much more significant. When sulfur is increased from 40 ppm to 330 ppm, we project that emissions increase by the following percentages:

<u>Vehicle Type</u>	<u>NMHC</u>	<u>NO_x</u>
LEV and ULEV LDV	40%	134%
LEV and ULEV LDT	24%	42%

These percentages apply to “normal emitting” vehicles, which generally are those in-use vehicles with emissions at or below twice their applicable emission standards. Higher emitting vehicles are projected to be less sensitive to sulfur, because the catalyst is not operating at peak efficiency in-use and should therefore be less affected on a percentage basis by higher sulfur levels.

We anticipate that Tier 2 vehicles will be at least as sensitive to sulfur as LEV and ULEV LDVs and possibly even more so, due to the greater stringency of the proposed Tier 2 emission standards, especially for NO_x. At present, however, we have only projected that Tier 2 vehicles will be just as sensitive as LEV and ULEV LDVs and not more so.

More detailed discussions of sulfur sensitivity can be found in the “EPA Staff Paper on Gasoline Sulfur Issues,”² published May 1, 1998, and the EPA report which developed sulfur sensitivity estimates for a range of vehicle classes for incorporation in the draft version of EPA’s fleet-wide emissions model, MOBILE6. This report is titled “Fuel Sulfur Effects on Exhaust Emissions”³ and is dated January 5, 1999.

Sulfur sensitivity has been shown to be variable and to depend upon both catalyst formulation and vehicle operating conditions, which are discussed in detail in both reports. Another variable, which was not discussed in either report, is the effect of real world vehicle aging with sulfur. Sulfur sensitivity is temperature dependent. Sulfur adheres to the catalyst surface more thoroughly at lower catalyst temperatures (approximately 450°C to 500°C) than higher temperatures. Several vehicle manufacturers have suggested that the sulfur sensitivity results from the numerous fleet studies actually underestimate the sensitivity of sulfur on exhaust emissions, because the test cycles (FTP or LA4 cycles) used to saturate the catalyst with sulfur result in catalyst temperatures that are too high. Specifically, the argument is that most vehicles achieve catalyst temperatures over the FTP that exceed 450°C, thus not allowing complete adsorption of sulfur to the catalyst surface, whereas real-world vehicle operation in metropolitan

Appendix B: Irreversibility of Sulfur's Emission Impact

non-attainment areas quite frequently result in catalyst temperatures at or below 450°C.

We have a sulfur test program currently underway to assess the validity of this concern. Although testing is still ongoing, very preliminary results from a single vehicle seems to support the fact that emissions are even more sensitive to sulfur when the catalyst is saturated with sulfur via on-road operation. We plan to have the results of this test program available prior to the development of technical analyses for the final rule. If the remainder of the testing supports the early results and manufacturer's contentions, real world levels of sulfur sensitivity would be even greater than the levels discussed above, further supporting the need for sulfur reduction in gasoline.

A second concern about the current estimates of sulfur sensitivity is that all of the vehicles in the test programs used to develop to above projections of sulfur sensitivities were only exposed to high sulfur fuel for a few miles of driving prior to emission testing. In addition to adsorbing onto the surface of the catalyst, sulfur can also penetrate into the precious metal layer, especially into palladium, and into the oxygen storage material. This penetration may not have fully occurred during the very few miles of operation prior to emission testing on high sulfur fuel. In an API sulfur reversibility test program discussed further below in this appendix, vehicles' sulfur sensitivity were measured after both short-term exposure to high sulfur fuel and after 1,000-2,000 miles of driving with high sulfur fuel. For the five vehicles tested, NMHC emission sensitivity was the same with both short-term and longer-term exposure to high sulfur fuel. However, NOx emission sensitivity was 25-50% higher after longer-term exposure to high sulfur fuel when compared to short-term exposure. Thus, the above sulfur sensitivities could significantly underestimate the impact of sulfur on NOx emissions for LEVs, ULEVs and Tier 2 vehicles. We plan to investigate this issue further in the future.

B. Theory Supporting the Reversibility and Irreversibility of Sulfur's Emission Impact

Sulfur impacts emissions from modern vehicles primarily by reducing the efficiency of the three-way catalyst. Molecules of sulfur (either in the form of sulfur dioxide or hydrogen sulfide) adsorb on the catalyst surface and basically take up space so that molecules of HC, CO and NOx cannot adsorb and react to form water, nitrogen, oxygen and carbon dioxide. With palladium catalysts, it appears that sulfur also penetrates into the metal itself, forming a reservoir of sulfur within the catalyst. Sulfur dioxide also penetrates into the oxygen storage medium of the catalyst and reduces the ability of the catalyst to manage the level of oxygen on the catalyst surface. This oxygen management function is a key component of the 98 percent plus efficiencies of today's three-way catalysts, particularly for controlling NOx emissions.

EPA summarized the basic chemical and thermodynamic mechanisms involved in sulfur's two types of interference in its staff paper on gasoline sulfur in May of 1998.⁴ This paper also summarized the conditions required to remove sulfur from the catalyst once the vehicle had

Tier 2/Sulfur Draft Regulatory Impact Analysis - April 1999

been exposed to high sulfur fuel. The results of a number of studies showed that generally high temperatures (in excess of 700° F) are required to remove sulfur from both the surface of the catalyst and from the washcoat matrix. In addition to high temperature, a rich exhaust (absence of oxygen coupled with presence of HC and CO, or a low air-fuel ratio) or an alternating sequence of rich and lean (presence of more oxygen in the exhaust than is needed to oxidize the HC and CO present, or a high air fuel ratio) exhaust was often needed to fully regenerate the catalyst. Larger degrees of lean and rich exhaust appear to be much more conducive to sulfur removal than small changes in air fuel ratio. When these rich or alternating rich-lean conditions were not present, even higher temperatures were required to remove the sulfur from the catalyst, when such removal was successful. However, when the combination of temperature and variation in the air-fuel ratio is sufficient, the sulfur accumulated from operation on high sulfur fuel appears to be essentially eliminated and the emission impact of the high sulfur fuel is fully reversed.

If sulfur reversibility was the only criteria involved in catalyst design, auto manufacturers could place their catalysts right up against the engine and design the onboard computer to vary the air fuel ratio from rich to lean sufficiently to regenerate the catalyst after any temporary exposure to high sulfur fuel. Engine exhaust temperatures are generally high enough at the exhaust manifold during typical driving to facilitate sulfur removal. The onboard computer is certainly capable of varying the air-fuel ratio significantly. However, other critical catalyst design criteria prevent such the use of such simple measures. First, excessive temperatures can thermally damage the catalyst and reduce its efficiency. Second, simultaneously high conversion efficiencies of HC, CO and NO_x require very tight air fuel ratio control (minimal swings to either rich or lean conditions).

Regarding catalyst temperature, auto manufacturers must balance a number of conflicting criteria. One important criterion for catalyst design is that it light-off quickly. Most of the HC and CO emissions from LEV vehicles, and significant amounts of NO_x emissions, occur prior to catalyst light-off. Achieving this has affected the type and amount of materials used in the catalyst and resulted in moving the catalyst closer to the engine. Many manufacturers have switched to catalysts containing palladium, which generally can withstand higher temperatures than platinum and rhodium catalysts. At the same time, catalyst manufacturers have improved the design of their platinum and rhodium catalysts so that they can withstand higher temperatures, as well. Moving the catalyst closer to the engine also increases catalyst temperature during warmed-up operation, other factors being equal. Despite improvements in the thermal durability of catalysts, sufficiently high temperatures can still cause a significant loss of catalyst efficiency.

Engine load also affects exhaust and catalyst temperature. The engine load for a given vehicle is a function of vehicle speed, rate of acceleration, vehicle weight and road grade, with higher levels of all of these factors leading to higher engine loads and catalyst temperatures. Vehicles which carry the most widely varying loads and which are driven the most aggressively will generally experience the most variation in their catalyst temperature. Manufacturers must

Appendix B: Irreversibility of Sulfur's Emission Impact

design their catalysts to both light-off quickly and stay warm under light loads while not sustaining thermal damage under heavy loads. Light trucks and sporty vehicles probably present the most difficult challenges in this regard. For example, light trucks are most often driven with one person and minimal cargo. However, they also are used to carry numerous passengers or carry or pull heavy cargo up steep hills. The catalyst must be designed to withstand the higher temperatures of these heavier loads.

One additional factor affecting catalyst temperature is the upcoming implementation of EPA and California SFTP standards. The SFTP standards address emissions generated while the vehicle is driving aggressively (high speeds and high rates of acceleration) and while the air conditioning is turned on, both of which generate higher engine loads than exist during EPA's FTP test cycle. Manufacturers have historically designed their engines to run rich under high loads. The excess fuel decreases exhaust and catalyst temperature relative to an engine running at stoichiometry (just the right amount of air to burn the fuel). The SFTP standards will require that manufacturers reduce much of this high-load enrichment in order to reduce HC and CO emissions during these high loads. Therefore, all other factors being equal, exhaust and catalyst temperatures under extreme conditions will increase after implementation of the SFTP standards, which begin their phase-in in the 2001 model year. Thus, the SFTP standards incrementally increase the difficulty of quickly lighting-off the catalyst while still protecting it from thermal damage during extreme driving conditions. While these extreme conditions must be considered in the catalyst design process, their frequency in-use is not sufficient to rely upon for sulfur removal. For example, some vehicle owners own and tow trailers up steep hills, while others do not. Therefore, while the SFTP standards may increase temperatures under some conditions, they will not necessarily increase sulfur removal capability for the general vehicle population.

Requiring manufacturers to increase the temperature of their catalysts under light loads to improve sulfur reversibility would therefore increase temperatures under heavy loads even further. EPA has not assessed the feasibility of manufacturers increasing warmed-up catalyst temperatures beyond that required by the current standards, as well as the proposed Tier 2 standards, without additional degradation in catalyst efficiency. However, based on the Johnson-Matthey data presented in the next section, even very high temperatures of 900° F are not necessarily sufficient to fully reverse the sulfur impact if extensive use of high sulfur fuel has occurred. Regular operation at such temperatures places the catalyst at risk of thermal damage from even occasional excursions above this level, which can regularly occur from the types of high load operation described above, as well as occasional spark plug misfire. Since the vast majority of the HC, CO and NO_x emission control occurring under both the current standards and the proposed Tier 2 standards relies on the proper operation of the catalyst over the life of the vehicle, increasing catalyst temperatures to enhance sulfur reversibility risks essentially all of the benefits of EPA's exhaust emission control program (both current and proposed). Therefore, it would be imprudent to require vehicle manufacturers to design catalysts that operate at temperatures high enough to improve the reversibility of sulfur effects and also meet the proposed Tier 2 standards in-use.

Tier 2/Sulfur Draft Regulatory Impact Analysis - April 1999

Moving to the variation in air-fuel ratio, manufacturers have significantly enhanced their engines' and computers' abilities over the past few years specifically to avoid large swings in rich and lean operations. This ability to maintain tight control of the air-fuel ratio has increased catalyst efficiency significantly in the process. Designing the vehicle to have alternating rich-lean operation may improve the reversibility of sulfur effects, but would reduce catalyst efficiency and potentially prevent the achievement of both current and proposed Tier 2 exhaust emissions standards. As was the case with increasing catalyst temperature, it would be counter-productive to reverse this progress in overall emission control just to enhance the sulfur reversibility of catalyst systems.

Thus, the two changes in emission control design, hotter catalyst temperatures and variable air-fuel ratios both run counter to other design criteria aimed at achieving stringent emission standards in-use. Therefore, EPA believes that sulfur reversibility should be evaluated with the catalyst temperatures and air-fuel ratio control of today's cleanest vehicles, considering the impact of the future SFTP standards. The next section will do this by evaluating the available sulfur reversibility data on such vehicles.

C. Results of Sulfur Reversibility Test Programs

EPA has received data from three test programs which evaluate the reversibility of sulfur's impact on vehicle emissions. These three programs are summarized in the following three sections. A fourth section summarizes other test data received, as well as describing some EPA testing which is underway.

1. Coordinating Research Council (CRC) Sulfur Reversibility Program

The CRC sulfur reversibility program evaluated six 1997 LEV LDV models that were part of their original sulfur sensitivity program. The following table lists the six vehicles used in the program.

Appendix B: Irreversibility of Sulfur's Emission Impact

Table B-1. CRC Test Vehicles

<i>Vehicle</i>	<i>Number of Cylinders</i>	<i>Engine Displacement</i>
Ford Taurus	6	3.0L
Ford Escort	4	2.0L
Honda Civic	4	1.6L
Toyota Camry	4	2.2L
Nissan Sentra	4	1.6L
Suzuki Metro	4	1.3L

All six vehicles were equipped with 100K mile bench aged catalysts and oxygen sensors. Testing was performed in two phases - I and II. Phase I consisted of three FTP tests (with a single LA4 cycle run in between) with an initial baseline fuel containing 30 ppm sulfur. Three additional FTP tests (again with the single LA4 preconditioning) were run using fuel containing 600 ppm sulfur. In order to evaluate the reversibility of the effects of the higher 600 ppm sulfur from the catalyst surface of the six vehicles, all of the vehicles ran eight FTP tests using an LA4 test just prior to each FTP as a sulfur “purge” cycle. The LA4 cycle was chosen as a purge cycle because of its general representativeness of city driving. Reversibility was defined as the ratio of 1) the difference between the average of emissions with high sulfur fuel and the average of emissions from the subsequent eight tests using low sulfur fuel to 2) the difference between the average of the high sulfur results with the average of the initial baseline low sulfur results. Total mileage accumulation during purge testing was roughly 250 miles. In other words, after 250 miles of operation, emission performance stabilized and no further purging of sulfur from the catalyst surface occurred.

Phase II consisted of three FTP tests with fuel containing 600 ppm sulfur followed by two FTP tests with 30 ppm sulfur fuel with an LA4 purge cycle prior to each FTP. Six FTP tests were then performed with a US06 cycle prior to each FTP as a sulfur purge cycle. The US06 cycle was chosen as a purge cycle to simulate aggressive high speed and load operation that would encourage higher catalyst temperatures and rich A/F operation. Reversibility was determined in the same manner as in phase I (same initial 30 ppm sulfur baseline). Total mileage accumulation turned out to be roughly 200 miles.

The following table lists the results of the CRC sulfur reversibility test program.

Table B-2. Sulfur Reversibility: CRC Test Program (%)

		<i>NMHC</i>		<i>NO_x</i>	
		<i>Purge Cycle</i>		<i>Purge Cycle</i>	
Vehicle Manufac	Models	LA4	US06	LA4	US06
Ford	Taurus	69.0	83.0	70.0	95.0
Ford	Escort	137.0	122.0	95.0	100.0
Honda	Civic	94.0	99.0	96.0	97.0
Nissan	Sentra	99.0	111.0	85.0	88.0
Toyota	Camry	112.0	98.0	50.0	102.0
Suzuki	Metro	170.0	165.0	86.0	87.0
Fleet Estimate		97.0	108.0	84.0	95.0

The fleet estimate used for the CRC data was determined by averaging the baseline low sulfur results, the high sulfur results and the final low sulfur results for all vehicles and determining reversibility as discussed above. These results indicate that on average, NMHC emissions are very reversible, regardless of purge cycle used (LA4 or US06). The Ford Taurus, however, showed only a moderate level of reversibility for NMHC, especially with the LA4 purge cycle (69 percent). The results for NO_x indicate that with the LA4 purge cycle, the average level of reversibility is 84 percent with the Toyota Camry having reversibility as low as 50 percent. When using the US06 purge cycle, NO_x emissions were far more reversible with an average reversibility of 95 percent. The Nissan Sentra and Suzuki Metro showed almost the exact same level of reversibility with both purge cycles.

2. American Petroleum Institute Sulfur Reversibility Program

The API program^a evaluated a total of seven vehicles, four were 1998 LEV LDVs, one was a 1998 ULEV LDV, and the other two were Tier 1 vehicles (LDV and LDT1). All of the

^a API has completed a third-party review of the results of their test program (as well as the CRC test program). See "Reversibility of Gasoline Sulfur Effects on Low Emissions Vehicles," T.J. Truex and L.S. Caretto for API, April 7, 1999.

Appendix B: Irreversibility of Sulfur's Emission Impact

vehicles had been driven for 6,000-10,000 miles, except for the S10 pickup, which had 50,000 miles on it. API replaced the catalysts of all of the vehicles. Reversibility of the sulfur effect was measured for all of these vehicles with their new catalysts thermally aged to the equivalent of 4,000 miles (i.e., low mileage catalysts) and after only a very short exposure to high sulfur fuel. Four of these vehicles were also tested with 1,000 miles of road aging on high sulfur fuel (540 ppm) prior to reversibility testing.

The sulfur reversibility of two vehicles was also tested after short term exposure to high sulfur fuel with their catalysts thermally aged to represent 100,000 miles of driving. (However, the oxygen sensors were not aged.) Finally, one vehicle was tested after 2,000 miles of driving using high sulfur fuel with its catalysts thermally aged to represent 100,000 miles of driving.

All of the vehicles were tested in a sequence similar to the one used by CRC. The program started with testing using low sulfur fuel (40 ppm). This was followed by testing with a high sulfur fuel (540 ppm). Then, the fuel was switched back to the low sulfur fuel and the vehicle operated over either an LA4 or US06 cycle, which was used as a sulfur purge cycle. Following this purge cycle, emissions were again measured with the FTP.

One major difference between the API and CRC programs was that API generally only performed two tests at each sulfur level, including the purge cycle phase. Thus, statistically speaking, the API program is weaker than the CRC program. Examination of individual emission test results shows significant variability occurred.

Table B-3 lists the vehicle tested in the API program.

Table B-3. API Test Vehicles

<i>Vehicle</i>	<i>Number of Cylinders</i>	<i>Engine Displacement</i>
1998 Ford Taurus (LEV)	6	3.0L
1998 Honda Accord (ULEV)	6	2.3L
1998 Toyota Avalon (LEV)	6	3.0L
1998 Nissan Altima (LEV)	4	2.4L
1998 Ford Grand Marquis (LEV)	8	4.6L
1998 Ford Town Car (Tier1)	8	4.6L
1997 Chevrolet S-10 (Tier1)	6	4.3L

Tier 2/Sulfur Draft Regulatory Impact Analysis - April 1999

API screened specific vehicles for this test program by performing emission testing over both the FTP and the US06 cycle. API believed that these vehicles were nearly in compliance with future SFTP standards and therefore representative of 2000 and later emission control technology. This will be discussed further below.

Table B-4 shows the sulfur reversibility emission results for all of the vehicles when tested with low mileage (4,000 mile) catalysts.

**Table B-4. Sulfur Reversibility: API Test Program
Low Mileage Catalysts, Short-Term Exposure to High Sulfur Fuel (%)**

		<i>NMHC</i>		<i>NOx</i>	
		<i>Purge Cycle</i>		<i>Purge Cycle</i>	
Vehicle Manufac	Models	LA4	US06	LA4	US06
Ford	98 Taurus	100.0	n/a *	96.2	n/a
Honda	98 Accord (ULEV)	23.1	100.0	78.3	97.8
Toyota	98 Avalon	71.4	42.9	52.1	106.3
Nissan	98 Altima	800	n/a*	125.0	n/a
Ford	98 Gr. Mar	103.2	80.6	84.5	71.8
Ford	98 Town Car (Tier1)	46.3	60.0	95.0	104.4
Chevrolet	97 S-10 (Tier1)	66.7	154.2	70.3	117.4
Fleet Estimate		67.9	45.9	83.3	92.3

* Vehicle not tested with US06 purge cycle.

The most obvious difference between the reversibilities measured by API and those found by CRC is that API's average NMHC reversibility rate when using the LA4 as a purge cycle is 68 percent, while CRC's average NMHC reversibility rate shows nearly full reversible at 97 percent. The measured NOx reversibilities (with the LA4 purge cycle) were almost identical in the two programs, 83 percent for API compared to 84 percent for CRC.

API found much higher reversibility using the US06 cycle as a purge cycle for NOx (92.3 percent). However, the opposite was true for NMHC (45.9 percent). This 45.9 percent reversibility is considerably lower than that found in the CRC program, where NMHC emissions were essentially fully reversible after purging with the US06 cycle.

Appendix B: Irreversibility of Sulfur's Emission Impact

Another difference between the API and CRC test results is the great deal of disparity between the reversibilities measured for individual vehicles in the API program. Some vehicles were highly reversible while others were not. The CRC results appear to be more consistent from vehicle-to-vehicle. This could be a result of the fact that CRC performed eight purge/FTP combinations with low sulfur fuel after exposure to high sulfur fuel, compared to API, which only performed two purge/FTP combinations. The CRC data showed that emissions after the switch back to low sulfur fuel fluctuated up and down before reaching a more consistent level during the eight tests. It is also possible that API simply experienced greater test-to-test variability, or that the vehicles in the API program simply differed more in their inherent reversibility.

Table B-5 shows measured reversibility for vehicles with low mileage catalysts that were operated on high sulfur fuel (540 ppm) for 1,000 miles on the road. Four vehicles were evaluated in this manner. The Taurus was tested with the LA4 purge cycle, but not the US06, while the Accord, Avalon, and Grand Marquis all were tested with the US06 purge cycle but not the LA4. As with the low mileage catalyst data, there is a significant amount of disparity between vehicles, especially for NMHC reversibility with the US06 cycle. Reversibility of NO_x emissions with the US06 cycle, however, are consistent and indicate that the sulfur effect is almost fully reversible with the US06 cycle. The Taurus with only short term exposure to high sulfur fuel was 100 percent reversible with the LA4 purge cycle for NMHC, but only 67.9 percent reversible with the LA4 cycle after road aging. Reversibility of NO_x emissions from the Taurus was nearly complete for both short term and longer term exposure to high sulfur fuel.

Table B-5. Sulfur Reversibility: API Test Program
Low Mileage Catalysts, 1,000 Mile Exposure to High Sulfur Fuel (%)

	<i>1,000 Mile Exposure</i>				<i>Short-Term Exposure</i>			
	<i>NMHC</i>		<i>NO_x</i>		<i>NMHC</i>		<i>NO_x</i>	
	<i>Purge Cycle</i>		<i>Purge Cycle</i>		<i>Purge Cycle</i>		<i>Purge cycle</i>	
Models	LA4	US06	LA4	US06	LA4	US06	LA4	US06
98 Taurus	67.5	102.5	97.6	169.0	100.0	n/a *	96.2	n/a
98 Accord (ULEV)	n/a	100.0	n/a	94.5	23.1	100.0	78.3	97.8
98 Avalon	n/a	75.0	n/a	101.4	71.4	42.9	52.1	106.3
98 Grand Marquis	n/a	45.5	n/a	101.9	103.2	80.6	84.5	71.8
Fleet Estimate	67.5	88.0	97.6	106.5	94.0	69.0	77.7	88.4

Tier 2/Sulfur Draft Regulatory Impact Analysis - April 1999

Table B-7 shows measured reversibility for vehicles with catalysts bench aged to represent 100,000 mile of driving. Only two vehicles were tested with this configuration - the Taurus and the Altima. Due to problems with the fuel tank on the original Altima used in the program, a second Altima was procured and tested with a 100K catalyst system. Reversibility of the Altima's emissions was measured after both short-term exposure to high sulfur fuel, as well as after 2,000 miles of highway driving with high sulfur fuel. This was the only vehicle in the API program that had both a 100,000 mile catalyst and extended road aging with high sulfur fuel. It was also the only vehicle with 2,000 miles of driving with high sulfur fuel instead of 1,000 like the other four vehicles with more extended use with high sulfur fuel.

Table B-6. Sulfur Reversibility: API with 100K Aged Catalysts Test Program (%)

	<i>NMHC</i>		<i>NOx</i>	
	<i>Purge Cycle</i>		<i>Purge Cycle</i>	
Models	LA4	US06	LA4	US06
Short-term Exposure to High Sulfur Fuel				
98 Taurus	207.0	107.0	88.7	85.4
98 Altima	84.9	102.7	78.9	89.2
Fleet estimate	120.0	104.0	87.3	87.3
2,000 Mile Exposure to High Sulfur Fuel				
98 Altima	n/a	115.1	n/a	93.9

The Taurus showed very similar levels of NMHC emission reversibility (after the LA4 purge cycle) with both low mileage and high mileage catalysts (essentially fully reversible in both cases). NOx emission reversibility dropped from 96.2 percent with the low mileage catalyst to 88.7 percent with the 100,000 mile catalyst. NOx emission reversibility did not improve after purging with US06 cycles.

The first Altima tested, which had a 4000 mile catalyst, was fully reversibility for both NMHC and NOx emissions with the LA4 purge cycle. The second Altima, which had a 100,000 mile catalyst showed less reversibility, only 84.9 percent for NMHC emissions and 78.9 percent for NOx emissions. Both NMHC and NOx emission reversibility improved with purging with the US06 cycle, though NOx emissions were still not fully reversible.

The second Altima showed similar NMHC and NOx reversibility with both short-term and long-term exposure to high sulfur fuel with the US06 purge cycle. The second Altima was

Appendix B: Irreversibility of Sulfur's Emission Impact

not tested with the LA4 purge cycle.

While the focus of the API test program was reversibility, the fact both short and longer term exposures to high sulfur fuel were evaluated also allows the comparison of sulfur sensitivity under these two conditions. Table B-7 presents the FTP emissions on both low and high sulfur fuel, the latter after both very short term exposure to high sulfur levels and 1,000-2,000 miles of driving on high sulfur fuel. All five vehicles so tested showed greater NO_x emission increases after exposure to high sulfur fuel for 1,000-2,000 miles than occurred after short term exposure. NMHC emissions, on the other hand, showed essentially the same sensitivity to sulfur after either short or longer term exposure. The increased NO_x emission sensitivity with extended mileage is a concern, as the sulfur sensitivity being projected for current and future vehicles was derived from testing which included only short term exposure to high sulfur fuel. The API data indicates that the effect of sulfur on NO_x emissions may be 30-50 percent greater than is currently being projected. EPA plans to investigate this further in the future.

Table B-7. Sulfur Sensitivity: API Test Program
Low Mileage Catalysts, Short-Term Exposure to High Sulfur Fuel (g/mi)

	<i>NMHC</i>			<i>NO_x</i>		
<i>FTP Test Sulfur Level</i>	<i>30 ppm</i>	<i>540 ppm</i>	<i>540 ppm</i>	<i>30 ppm</i>	<i>540 ppm</i>	<i>540 ppm</i>
Sulfur Exposure	---	Short-term	1,000 Mile	----	Short-term	1,000 Mile
Vehicle	Low Mileage Catalysts					
Taurus	0.033	0.051	0.073	0.075	0.101	0.117
Accord	0.029	0.036	0.041	0.100	0.164	0.245
Avalon	0.040	0.058	0.060	0.068	0.130	0.143
Gr. Marq.	0.044	0.075	0.055	0.040	0.143	0.152
Average	0.037	0.055	0.057	0.071	0.135	0.164
	100,000 Mile Catalysts					
Altima	0.041	0.059	0.057	0.061	0.112	0.132

3. Johnson Matthey Sulfur Reversibility Program

Johnson Matthey (JM), a catalyst manufacturer, conducted a test program to evaluate if

Tier 2/Sulfur Draft Regulatory Impact Analysis - April 1999

long term exposure to high sulfur fuel damaged catalysts, whether the damage was reversible when the system was run on low sulfur fuel, and to determine whether exposure of catalysts to higher temperatures with low sulfur fuel reversed the damage. Four catalyst designs: Palladium (Pd), Pd/Rhodium (Rh), Platinum (Pt)/Rh, and Pt/Pd/Rh, were bench aged for 45 hours approximately equal to 50K miles. There were two sets of catalysts. Set A was aged using 87 ppm sulfur, while set B was aged using 735 ppm. Set A was always used as the baseline test. Set B was used to measure high sulfur results (735 ppm) and the consequent low sulfur results. A single vehicle was used for all of the testing - a 1990 Tier 0 Mitsubishi Galant. Each catalyst was installed on the vehicle and then evaluated. Each catalyst was located in a front underbody position. Sulfur purging with the US06 cycle was not evaluated, only the LA4 purge cycle.

After evaluating reversibility performance of each catalyst to exposure of low sulfur fuel, JM attempted to demonstrate the effect prolonged exposure to high catalyst temperatures would have on sulfur reversibility, since most of the scientific literature has suggested that exposing the catalyst system to temperatures over 700° C should facilitate reversibility. Each catalyst was run over a steady-state sulfur recovery cycle which involved an A/F ratio (AFR) oscillation of stoichiometry +/- 0.5 AFR @ 0.10 Hz (5 seconds rich/5 seconds lean) and a catalyst bed temperature of 700° C. This procedure was followed by a cycle at 800° C and then a final cycle at 900° C. What JM found was that according to their results, sulfur is highly irreversible even when the catalyst is exposed for five straight hours to temperatures of 700° C, 800° C, and 900° C.

Table B-8 lists the results of JM's sulfur reversibility program. The fleet estimate is also a simple arithmetic average of the data. It should be noted that all of the catalysts had very poor reversibility when only switching back to low sulfur fuel. As the catalysts were then exposed to increasing temperature, the results became mixed - some catalysts improving, while others deteriorated. For NMHC, the Pt/Rh catalyst appears to be the only catalyst that showed more reversibility in response to increased temperatures. Curiously, most of the catalysts seemed to respond best to the 700° C and 800° C temperatures and poorly to the highest temperature (900° C). For NOx, the results were even poorer. For example, the Pd/Rh catalyst never experienced a NOx sulfur reversibility rate above 18 percent. In fact, most of the time it had negative reversibility rates, meaning once the catalyst was re-exposed to low sulfur fuel after having been operated on high sulfur fuel, the low sulfur emission results were higher than the high sulfur results.

Appendix B: Irreversibility of Sulfur's Emission Impact

Table B-8. Sulfur Reversibility: Johnson Matthey Test Program (LA4 Purge Cycle) (%)

Catalyst	NMHC				NOx			
	Sulfur Purging Temperature							
	None	700° C	800° C	900° C	None	700° C	800° C	900° C
Pd	50.0	50.0	66.0	17.0	44.0	75.0	88.0	69.0
Pd/Rh	30.0	30.0	20.0	10.0	-5.0	18.0	-50.0	-33.0
Pt/Rh	50.0	92.0	92.0	83.0	32.0	32.0	32.0	32.0
Pt/Pd/Rh	38.0	85.0	46.0	54.0	47.0	65.0	-35.0	47.0
Fleet Estimate	42.0	64.3	56.0	41.0	29.5	47.5	8.8	28.8

4. Other Testing

Honda has suggested that in order for complete sulfur adsorption onto the catalyst surface, catalyst temperatures must be below 500° C. Honda believes that the cycles that have been used in the various sulfur test programs to adhere the sulfur to the catalyst surface have been inadequate. They believe catalyst temperatures over the FTP or LA4 test have generally been exceeding 500° C at some point or another during the cycle. They proposed a conditioning cycle that consisted of an extended 35 mph cruise making sure the catalyst temperature does not exceed 450° C - 500° C. Full sulfur adsorption is determined by monitoring feedgas SO₂ and exhaust SO₂ until they are the same. Honda found that when using their conditioning cycle, NMHC emissions were 20 percent more irreversible than when using the FTP or LA4 for sulfur conditioning. NO_x emissions were 19 percent more irreversible.

As a result of Honda's information, the 1K road aging results from the API program, and the apparent effect of sulfur aging on the JM results, we have undertaken our own EPA sulfur reversibility evaluation program. The primary focus of our program is to determine the effect road aging has on sulfur adsorption to the catalyst and the subsequent removal or reversal of the sulfur. At this time, testing is still underway and we are just about to start the road aging. Although this data will not be available for the NPRM, it will be completed in time for the final rule.

D. Criteria for Evaluating Sulfur Reversibility Data

Projecting the degree of sulfur irreversibility for various vehicles types under representative in-use conditions is difficult due to inadequacies in essentially all of the available data. As mentioned in the previous section, the sulfur reversibility testing would ideally have

Tier 2/Sulfur Draft Regulatory Impact Analysis - April 1999

used vehicles designed to meet a range of FTP and SFTP standards, thermally aged catalyst systems prior to testing, exposed these systems to high sulfur fuel for a few thousand miles of typical driving, and used representative driving cycles to purge sulfur between emission tests.

While many of the vehicles tested had thermally aged catalyst systems, none were designed to meet SFTP standards. API tested the vehicles in their test program over the US06 cycle to assess the degree to which they might already be in compliance with future SFTP standards. The results showed that two out of the eight (including the second Altima) vehicles were below the 0.14 g/mi US06 NMHC+NO_x standard for LEVs and ULEVs, while half of the vehicles were below the 8.0 g/mi US06 CO standard. However, only one vehicle met the NMHC+NO_x standard with any significant margin of safety. Thus, this screening data does not support the contention that these vehicles were essentially in compliance with the SFTP standards. Also, API did not measure emissions over the SC03 cycle, which simulates emissions with the air conditioning system turned on and which is also a part of the SFTP requirement. Thus, there is no evidence that these vehicles were designed to meet non-US06 related SFTP requirements.

In addition to US06 emission data, API also measured each vehicle's air-fuel ratio on a second-by-second basis over both the FTP and US06 cycles. The standard deviation of the air-fuel ratio over the FTP averaged 0.35, while that over the US06 cycle averaged 1.03. Thus, variability in air-fuel mixture control was nearly three times as great over the US06 cycle as over the FTP. Tight air-fuel mixture control is essential to maintaining low engine-out emissions and high catalyst over the entire emission test and during in-use driving. The first step a manufacturer will take in order to comply with the SFTP requirements will be to modify the engine calibration to achieve the best level of air-fuel mixture control possible. The fact that these vehicles showed much greater variability over the US06 cycle indicates that manufacturers had not yet begun the process of making these vehicles SFTP-compliant. Previous studies have shown that wide swings in air-fuel ratio reduce the impact of sulfur on catalyst efficiency and emissions relative to minor swings in air-fuel ratio. Thus, this criterion appears to be of critical importance in projecting the reversibility of SFTP-compliant LEVs and Tier 2 vehicles.

Moving to exposure to high sulfur fuel, while a few vehicles were operated on high sulfur fuel for a thousand miles or more, only two vehicles had catalysts which were thermally aged to more than a few thousand miles. Also, the driving cycles used to purge sulfur after switching from high to low sulfur fuel were not any of the driving cycles developed to be fully "representative" of recent driving patterns. The result of these shortcomings is that considerable technical judgment has to be used to project the degree of sulfur irreversibility which would occur for both current and future vehicles.

EPA established a number of criteria for evaluating the available data in order to project likely levels of in-use sulfur reversibility. The first criterion is to focus exclusively on testing of vehicles with thermally aged catalysts. We believe that this is essential, because catalysts prior to thermal aging contain far more surface area and oxygen storage capacity than is needed to meet

Appendix B: Irreversibility of Sulfur's Emission Impact

low emission levels. It is possible for sulfur to deactivate a considerable portion of the surface area and oxygen storage with minor impacts on overall catalyst performance. This would not be representative of the impact of sulfur on real-world emissions over most of the vehicle's life.

The second criterion is to give priority to testing where the catalyst has been exposed to high sulfur for a considerable period of time. Long term exposure would be the predominant mode of exposure under a regional sulfur program such as that proposed by API. With the high sulfur region being potentially quite large geographically, most vehicles entering it are likely to be there awhile. Simply crossing the region that would have 300 ppm average sulfur levels under the regional program proposed by API represents roughly 1000 or more miles.

Under any sulfur control program, sulfur levels will vary from batch to batch of gasoline produced by refineries. For example, under the proposal, sulfur could easily vary from less than 10 ppm to 80 ppm in-use after 2008. Under this scenario, exposure to high sulfur fuel could be one tankful at a time, or could continue for several tankfuls, depending on the production patterns at refineries and the purchasing patterns of individuals. Still, even one tankful of fuel typically lasts 300 miles or more. This is far more than the 10-20 miles of exposure to high sulfur fuel which occurred in most of the testing summarized in the previous section.

Development of the subsequent criteria are more complex, because the issues of SFTP compliance and representative driving cycles are not as easily addressed. None of the vehicles tested were certified to either the Tier 1 or LEV SFTP emission standards. While some of the vehicles may have SFTP emissions close to or even below the applicable SFTP standards, it is still likely that manufacturers would change their engine calibrations to enhance compliance with these emission standards in-use. This is confirmed by the API measurements of air-fuel ratio over the FTP and US06 cycles. Thus, none of the test vehicles can be assured of having SFTP-compliant engine calibrations.

Likewise, only the LA4 and US06 driving cycles were used in the test programs performed to date. The LA4 cycle was derived from driving patterns in Los Angeles in the early 1970's. However, due to physical limitations in the dynamometers in use at the time, all accelerations greater than 3.3 mph per second were reduced to this level. This, plus the fact that driving has become more aggressive over the past 25 years makes the LA4 cycle less aggressive on average than today's typical driving. However, the LA4 cycle does include driving as fast as 58 mph, so it is also not representative of light, city driving.

The US06 cycle is made up of real-world driving segments.^b However, the concentration of aggressive driving is much higher than occurs in the real world. Therefore, the length of time

^b All but one of the segments were taken from EPA's REP05 cycle, which represents the aggressive portion of in-use driving. The remaining segment was taken from ARB's HL07 cycle, which was intended to represent aggressive in-use driving in California.

Tier 2/Sulfur Draft Regulatory Impact Analysis - April 1999

that the catalyst is exposed to both high temperatures and rich conditions is much higher than would occur in the real world. This could easily remove more sulfur than would be removed in-use even during aggressive driving.

As mentioned in Section B, meeting the SFTP standards will require the tightening of air-fuel mixture control and reduce the amount of rich operation in-use during aggressive driving. Both of these changes directionally reduce sulfur removal. This primarily affects the sulfur reversibility testing after preconditioning with the US06 cycle. In particular, it casts considerable doubt in the applicability of measured reversibilities using the US06 purge cycle to SFTP-compliant vehicles. Therefore, the measured levels of sulfur reversibility after operation on US06 cycles will not be used to project the in-use levels of sulfur reversibility for SFTP-compliant vehicles.

For pre-SFTP vehicles, the US06 cycle still likely over-estimates the amount of sulfur reversibility which would occur in-use, due to its unrepresentative concentration of high temperatures and rich operation. Thus, the measured levels of sulfur reversibility after operation on both LA4 and US06 cycles will be used to project the in-use levels of sulfur reversibility for pre-SFTP vehicles.

In summary, the projections developed in the following section will:

1. Only use data from vehicles with aged catalyst systems,
2. Emphasize data from vehicles whose catalysts experienced substantial use with high sulfur fuel,
3. For projections regarding SFTP-compliant vehicles, only use data where the sulfur was purged using the LA4 cycle, and
4. For projections regarding pre-SFTP vehicles, use data where the sulfur was purged using either the LA4 or US06 cycle.

E. Projected Levels of Sulfur Irreversibility In-Use

Applying the first criterion developed in Section D. results in the retention of the CRC and JM data (Tables B-2 and B-8), as that testing was performed on vehicles with thermally aged catalysts. It also allows the use of the API data contained in Table B-6. However, the remaining API data apply to vehicles with low mileage catalysts, which are not sufficiently representative of in-use operation. Therefore, EPA's current conclusions about reversibility of sulfur effects do not rely on the API data except that in Table B-6.

Of these data, only the JM data and the second Altima tested by API also involved extensive use of high sulfur fuel prior to the measurement of reversibility. JM simulated the use of high sulfur fuel through oven aging, so it may not be fully representative as actual vehicle driving on the road. However, oven aging to simulate on-road thermal degradation is well

Appendix B: Irreversibility of Sulfur's Emission Impact

established, so the same for sulfur aging should be equally acceptable.

API actually drove the second Altima on the road for 2,000 miles with high sulfur fuel. However, the type of driving actually performed is not known, raising some uncertainty about its representativeness. More importantly, API only measured reversibility with this vehicle after operating the vehicle with low sulfur fuel over the US06 cycle. This took advantage of the vehicle's widely varying air-fuel ratio over this test cycle and likely purged more sulfur off of the catalyst than would occur with an SFTP-compliant vehicle. JM, on the other hand, simulated the type of air-fuel ratio control which would be indicative of an SFTP-compliant vehicle with it oven aging and purging. Thus, overall, the JM data should receive the greatest weight in this analysis. Table B-9 summarizes the results of these three test programs.

Table B-9. Sulfur Reversibility: Summary of Relevant Test Programs (%)

	<i>NMHC</i>		<i>NO_x</i>	
	<i>Purge Cycle</i>		<i>Purge Cycle</i>	
Models	LA4	US06	LA4	US06
CRC (6 vehicles)	97%	Complete	84%	95%
JM (4 catalysts)	4-64%	41-64%	30-48%	9-48%
API (2-3 vehicles)	Complete	Complete	87%	89%

The JM results are shown as a range, as it is difficult at this time to average the results at the various sulfur purging temperatures. However, the JM data were placed into the two purge cycle categories by assuming that the test results with no oven-based sulfur purging and the purging at 700° C were similar to LA4 driving, while the results with oven purging at 700-900° C were similar to US06 driving. Another relevant factor is that the results of the API testing are the most erratic, primarily due to the relatively small number of replicate tests.

As can be seen, there is considerable variation in the measured levels of sulfur reversibility in the above test data. In particular, the JM data show much less reversibility and should be given the most weight because it was the only test program thus far to include catalysts aged both thermally and with high sulfur fuel. Therefore, the overall projection of reversibility primarily hinges on the relative weight given to the JM data. In any event, there will be considerable uncertainty in any summary projection developed from these results, because of the limitations in the test methods described above.

For pre-SFTP vehicles, we decided to utilize reversibility measurements using both the LA4 and US06 driving cycles. Since the CRC and API vehicles are pre-SFTP vehicles, these

Tier 2/Sulfur Draft Regulatory Impact Analysis - April 1999

two test programs were given considerable weight along with those of JM. For these vehicles, we project that NMHC emissions are fully reversible, while NOx emissions are only 85 percent reversible. For SFTP-compliant vehicles, we decided above to utilize reversibility measurements using only the LA4 driving cycle. We also gave additional weight to the JM data, as the vehicles tested in the CRC and API programs were not SFTP-compliant. While the JM test vehicle was also not SFTP-compliant, the purging of the sulfur from the catalyst was conducted in a way that was more consistent with that of an SFTP-compliant vehicle. Given this, we project that both NMHC and NOx emissions from SFTP-compliant vehicles, will be 50 percent reversible. Based on the average results of the three test programs, we could have projected a higher reversibility for NMHC emissions and a lower reversibility for NOx emissions. However, examining the results for the individual vehicles and catalysts and given the fact that none of the vehicles tested were SFTP-compliant, we decided to project a single level of reversibility for both pollutants.

Appendix B: Irreversibility of Sulfur's Emission Impact

Appendix B. References:

1. "Development of Light-Duty Emission Inventory Estimates in the Notice of Proposed Rulemaking for Tier 2 and Sulfur Standards," U.S. EPA, February 1999.
2. "EPA Staff Paper on Gasoline Sulfur Issues," U.S. EPA, May 1998, EPA420-R-98-005.
3. EPA Report Number M6.FUL.001
4. "EPA Staff Paper on Gasoline Sulfur Issues," U.S. EPA, May 1998, EPA420-R-98-005.